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Present Status and Future Prospects of the Metallurgy of Zinc: Electrolytic Zinc

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Present Status and Future Prospects of the Metallurgy of Zinc.

A symposium before the New York Sections of the American Electrochemical Society and the American Institute of Mining Engineers.

The joint meeting of the New York sections of the American Institute of Mining Engineers and of the American Electrochemical Society held on the evening of November 20 in the Engineering Building was well attended, there being some 200 members present, and the carefully arranged program deserved the interest which was shown.

There were three papers. Mr. George C. Stone presented a very careful review of the improvements which have been attained in the metallurgy of zinc with the time-honored retort process; Mr. W. R. Ingalls discussed the possibilities and limitations of electric zinc smelting, while Dr. J. W. Richards dealt with electrolytic zinc, having stepped in at the last minute to cover this phase of zinc electrometallurgy, as a promised paper by Dr. Victor Englehardt, of Germany, on this subject, had not arrived in time.

Mr. Lawrence Addicks, chairman of the New York Section of the American Electrochemical Society, presided during the presentation of the three papers. Mr. L. D. Huntoon, chairman of the New York Section of the American Institute of Mining Engineers, presided during the discussion.

Improvements in the Retort Process

Mr. **George C. Stone,** of the New Jersey Zinc Company, in reviewing in a most interesting manner the development of the retort process, emphasized that while no spectacular or radical changes had been worked in the metallurgy of zinc as in the metallurgy of iron and copper by the introduction of converters, yet the progress had been as great with zinc as with the other common metals.

Three essential facts limit the possible apparatus for the production of zinc.

First, the temperature at which zinc is reduced by carbon is much above the volatilizing point of the metal, and it is, therefore, always produced as a vapor.

Second, to obtain a merchantable product the vapor must be condensed at a temperature well above the melting point of the metals. The temperature of the condenser must be close to the boiling point of zinc (920°) nearest to the retort and very much lower at the other end, because the condensation temperature depends on the concentration of zinc in the vapor and is lower the more dilute the vapor. The vapors are rich in zinc when they enter the retort and low in zinc when they leave it.

Third, the reaction by which zinc oxide and carbon monoxide are changed into metallic zinc and carbon dioxide is reversible. The reduction of zinc proceeds only until there is a certain ratio of carbon dioxide of zinc in the atmosphere and then stops, and in order to effect complete reduction there must be an excess of carbon always present.

These three essential facts control the type of apparatus to be used. It must be a closed chamber. It must be heated externally because the gas from the heating fuel must not come in contact with the charge. As the mixture of ore and coal forming the charge is a poor conductor of heat the size of the chamber containing it must be small in at least one direction or the heating will be too slow. The charge must, at all stages, contain a large excess of carbon to reduce at once all CO_2 formed. The condensers should be as close to the charge as possible and as small as will do the work in order to make it possible to maintain the proper heat gradient in them. The condensers must be kept within proper limits of temperature, diminishing towards the exit.

Mr. Stone explained in some detail why he questioned the statement commonly made that his spelter furnace is extravagant in heating, and then summed up the progress made in recent years as follows:

Forty or fifty years ago the typical Belgian furnace contained from fifty to ninety retorts of about 0.8 of a cubic ft. capacity each. At the present time the furnaces used in the natural gas field contain from 500 to 700 retorts of about 1.4 ft. each, an increase in capacity of about 1300 per cent. Furnaces containing 1008 retorts are in operation doing satisfactory work; this is an increase of about 2400 per cent in size and capacity. The increase in capacity of the spelter furnaces is, therefore, about the same as that of the modern coke furnace making pig-iron over the old charcoal furnaces.

Mere increase in size, however, does not amount to much unless accompanied by increased efficiency. In this respect the zinc furnaces show well. In the iron furnaces there has been no improvement in the proportion of metal recovered, the old furnaces having given almost theoretical results. With zinc the improvement has been very marked. In 1844, at the Vieille Montagne works, the recovery was about 62 per cent, and even as late as 1880 a recovery of 75 per cent was considered good work. To-day 87 per cent is only fair, and many works can show runs of long periods averaging 90 per cent and over.

The fuel consumption has been decreased largely mainly by the adoption of regenerative gas-firing. Even in direct-fired furnaces the decrease is large. Comparing furnaces only using the same kind of coal, where the hand-fired furnaces twenty years ago required 3, 3½ and even 4 tons of coal per ton of ore, well-equipped gas furnaces using the same coal, and working the same class of ore, now take only 1½ to 1¾ tons.

Labor has also been largely reduced. The old Belgian furnaces required five days' labor per charge, two men working twenty-four hours continuously, and an extra helper on the day shift only. As these furnaces worked only about a ton of ore they required five days' labor per ton. At present all twenty-four-hour work is done away with, and not over 1½ days' labor is required per ton.

In 1844 fifteen to twenty days was the usual life of a retort. Now good retorts made in hydraulic processes last from thirty to forty days, and at that more are replaced because they are filled up than because they leak.

Mr. Stone believed progress would continue to be made rather on the lines of improvement in the present retort process than by the adoption of radically different ones. He finally discussed briefly three different new types of processes which have been proposed, namely, the wet, electrolytic, and electrothermic.

One main reason for the lack of success of the wet process is the difficulty of dissolving the zinc. Zinc blende usually contains a large amount of iron and when roasted the zinc and iron combine to form zinc ferrite, which is practically insoluble in either acids or alkalies under economic conditions. The purification of the solution is also expensive and rather troublesome.

Electrolytic zinc of excellent quality has been made by one firm for several years, but they have never increased the original plant. It is generally believed that this plant is only possible in connection with other operations carried on by them. Besides other difficulties of wet processes Mr. Stone said that electrolytic processes have the trouble of large power requirements.

Electric smelting of zinc ores is seriously limited in this country by the fact that in most mining districts electric power cost is high. Further, there are condensation troubles and other difficulties.

Mr. Stone concluded that the present types of furnaces can be much improved. Fuel can be saved by better design and proportions of regenerators; better arrangement of the ports and decreasing radiation losses by more thorough lagging of the parts of the furnaces from which radiation is purely wasteful. A determination of the best size and shape of retort and condenser for different ores, and the choice of such as suit the particular ore to be worked instead of using one size and arrangement for all, will give improved results in recovery and output. A careful study and application of the principles on which ores should be mixed offer a wide field for improvement.

Electric Zinc Smelting

Mr. **W. R. Ingalls'** discussion of the possibilities of the electric furnace for zinc smelting was very careful and conservative. Mr. Ingalls said he was neither a pessimist nor an optimist with respect to electric zinc smelting, but an agnostic. He agreed that electric zinc smelting was no longer in the laboratory stage and referred to some enlargements now being made in the electric zinc furnace plants of Norway. He thought reckless talk had held back the development of electric zinc smelting.

At considerable length Mr. Ingalls discussed the well-known condensation troubles, blue powder being obtained instead of spelter.

The fire-smelting process is a two-stage intermittent process of heating up and distillation. The electric smelting process is intended as one continuous operation. This distinction causes important differences.

The condensation troubles originate at least partly in the furnace itself. Mr. Ingalls distinguished between two kinds of blue powder—meltable and non-meltable. The fact that the condenser is too cold may account in part for meltable blue powder, while non-meltable blue powder is due to impurities in the vapor to be condensed—if it contains carbon dioxide, volatilized lead, dust and other impurities. Oxidized lead is often found in large extent in blue powder.

As to the different electric furnace designs for zinc smelting, Mr. Ingalls could not see any great difference between them. He thought there was not much in electric zinc smelting at present beyond visions and ideas. There were few figures and the subject was attracting attention chiefly on account of its mystery.

Mr. Ingalls then compared the different items of cost of electric smelting and retort smelting. But few of the items in question were known besides the cost of electric power as against coal. He thought the consumption of 1200 kw hours per ton of ore to be plausible though hardly yet an accomplished fact. As to the comparative cost of retorts and electrodes, he maintained his former statement that nobody can yet say which will be the weaker. If the cost sheet of the Trollhättan plant was refigured by inserting American for Scandinavian prices the cost of the application of the process would be found to be absolutely prohibitive.

Mr. Ingalls concluded that electric zinc smelting was still very much in its infancy and that at the present time all we could say was that we did not know.

Electrolytic Zinc

Dr. **Joseph W. Richards** then discussed electrolytic zinc. In order to show the variety of processes which have been devised in this field he gave a brief outline of the contents of Guenther's German book on the subject. He then took up recent developments with reference to a lecture by Dr. Victor Engelhardt which was published in abstract in our January issue, 1913 (Volume XI, page 43).

While Dr. Engelhardt considers the mere refining of commercial zinc analogous to copper refining, to be economically absurd, Dr. Richards thought it might be possible, under favorable conditions. It would, of course, be necessary to keep the solution clear. It can be kept free from iron by bubbling air through it, whereupon it should be filtered clear. Such an electrolytic refining process might be particularly advantageous if carried out for electroplating purposes.

Engelhardt had stated with regard to direct processes using soluble anodes containing zinc that many attempts had been made since 1880 to utilize the energy due to the solution of the anode and to prepare anodes containing various zinc compounds mixed with coke or coal powder with and without pressure with various binding materials, etc. All such processes have proven a failure. Dr. Richards thought, however, that packing the ore around an insoluble anode (instead of incorporating it in it) was a possibility. He then commented briefly on Engelhardt's description of the latest Siemens & Halske process with insoluble anodes and finally discussed broadly the scheme of sulphate roasting.

Dr. Richards thought that sulphate roasting was essentially a misconception. One gets a dilute solution of sulphuric acid which must be dispensed with after all the zinc is gotten out, and the sulphuric acid produced is a source of trouble.

The correct way to work is, according to Dr. Richards, to roast the ore to oxide as nearly as practical. It is then leached with sulphuric acid and electrolyzed in a double compartment electrolytic cell, zinc being deposited on the cathode and sulphuric acid is then used for leaching another quantity of roasted oxide ore whereby the acid is neutralized. The zinc sulphate thereby obtained is again electrolyzed, etc. In this process, therefore, the sulphuric acid passes continuously through this cycle. It is formed in the electrolysis, neutralized in leaching, again formed in electrolysis, etc. The first supply of sulphuric acid is obtained from the roast furnace gases. This principle is used in a plant at Butte, Montana.

Discussion

Dr. **C. F. Chandler** opened the discussion with a characteristic little speech. When the chairman, Mr. Huntoon, called him up Dr. Chandler said: "My old pupil gets even with me. He knows I am not prepared, and that is why he calls me up." He then spoke briefly on two occasions in his career when he got into connection with zinc—the first time, 50 years ago, in a poison-murder case, where he had trouble to get zinc free from arsenic, and the second time, later on, in a lawsuit on electrolytic zinc.

Mr. **Woolsey McA. Johnson** was then asked to give a review of his work on electric zinc smelting at Hartford, Conn. With respect to Mr. Ingalls' statement that a power consumption of 1200 kw hours per ton of ore was plausible and pretty good, Mr. Johnson said this would not be the minimum, but rather the maximum consumption he would consider acceptable. With a small furnace running with 25 per cent efficiency he had usually an energy consumption of 1400 kw hours per ton of charge, but he had also done it at 900 or 1000 kw hours. With a larger furnace he was sure to get a much higher efficiency and reduce the energy consumption correspondingly.

As to the electrode consumption this was 6½ to 7 pounds of electrode carbon per 1000 kw hours, and he figured the cost of electrodes was considerably less than the corresponding expense for zinc retorts.

Mr. Johnson thought that the field of the electric furnace was not so much for plain zinc ores as for complex sulphide ores and by-product recovery must be considered if we want to see what electric zinc smelting can do and will do.

About roasting, Mr. Ingalls had expressed the opinion that the cost would be about the same for electric smelting and for the retort process. But Mr. Johnson pointed out that with the electric furnace it is by no means necessary to dead-roast the ore. Roasting down to 4 per cent of sulphur is about right for the electric zinc furnace. Sometimes in the Hartford plant they add green ore to get a matte. They do not want it to be too metallic and, therefore, add sulphur. This point should make a big difference in the cost of roasting for electric smelting and retort smelting. There is a vast metallurgical difference between a roast to half of 1 per cent and a roast to 4 or 6 per cent, both with respect to capital cost of the roasting furnace and with respect to the cost of roasting. Nine-tenths of all roasting troubles is caused by removing the last 40 or 50 lbs. of sulphur. This point also has a distinct bearing on the sulphuric acid plant for the reason that a richer gas is made. Mr. Johnson said that they are now building a three-ton furnace at Hartford, and he would be glad to show it to visitors. "Zinc comes from Missouri, and you have to show people."

Mr. **Alfred H. Cowles** spoke of some experiments made by him many years ago on electrolytic zinc. One difficulty which he encountered was the high resistance of the zinc sulphate solution; this was overcome by putting the electrodes close together by the use of two drums. The zinc deposited on the wires could be easily scraped off. The process used was cyclic with respect to sulphuric acid as described in Dr. Richards' paper.

The chief difficulty which was encountered was the melting

together of the finely divided zinc deposit. They tried for half a year all kinds of fluxes, but were unsuccessful until they found that it could be quite easily done with zinc chloride. It would be worth while to try this in the blue powder difficulty. The use of zinc chloride is not patented. Mr. Cowles pointed out that in comparison with aluminium production about one-seventh of the amount of energy is required to deposit a pound of zinc as is necessary to deposit a pound of aluminium.

Mr. **H. A. Wentworth** asked whether any unmeltable blue powder was formed at the higher temperature before the fumes reached the condenser at all. Mr. Ingalls said that he had no evidence to that effect and thought that the blue powder was formed in the condenser.

Dr. **J. W. Richards** referred to Mr. Ingalls' statement that there was no great difference between different electric zinc furnaces. While this might appear to be so at first glance, Dr. Richards insisted that there was a very great and important difference if the matter was investigated more in detail and the differences in the furnace designs had a great deal to do with the condensation problem. In the DeLaval type of furnace the fumes acted as resistor, and were thereby overheated, which increased the condensation difficulties considerably. On the other hand, a furnace using a buried arc or smothered arc was better, but it had zones of high temperature, and within these zones there was liability of evaporation of materials like silica or silicon which would later cause condensation troubles. But, in the whole, this type of furnace had certain advantages over the type in which the fumes acted as resistor. Finally, in resistance furnaces of the Clerc type or the Queneau type the conditions seemed to be quite different and probably more favorable.

Mr. **E. G. Spilsbury** emphasized that zinc is produced in the retort furnace not so much by contact with carbon monoxide gas, but by actual contact with elemental carbon itself. He recited some unsuccessful experiments which he had made some years ago on the use of carbon monoxide gas as reducing agent.

Mr. **Woolsey McA. Johnson** said that they had overcome their condensation troubles largely. Their average condensation factor (the ratio of weight of zinc in spelter produced to the sum of weight of zinc in flue dust plus ladle skimmings plus blue powder plus spelter) at Hartford was 75 per cent. They produced 1 to 5 per cent of blue powder and 15 to 20 per cent of flue dust. He emphasized that a sharp distinction should be made between blue powder and flue dust. One form of blue powder was particularly troublesome, namely, that due to the reaction between zinc and SO_2 or sulphur from the matte, and referred to his Canadian patent allowed February, 1913, in which a metallurgical description of "sulfidized chemical" blue-powder and ways of preventing its formation is clearly given.

After a vote of thanks, proposed by Professor Kemp and seconded by Mr. Stoughton, to the speakers of the evening and to the Committee of Arrangements, the meeting adjourned. It was followed by an enjoyable informal social gathering in the rooms of the Institute of Mining Engineers.